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Samuel Drouet, Areej Merhi, Guillaume Grelaud, Marie P. Cifuentes, Mark G. Humphrey, et al.. Enhanced two-photon absorption cross-sections of zinc(II) tetraphenylporphyrins peripherally substituted with d(6)-metal alkynyl complexes. *New Journal of Chemistry*, 2012, 36 (11), pp.2192-2195. 10.1039/C2NJ40589J . hal-00855371

HAL Id: hal-00855371

<https://hal.science/hal-00855371>

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Cite this: *New J. Chem.*, 2012, **36**, 2192–2195

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Enhanced two-photon absorption cross-sections of zinc(II) tetraphenylporphyrins peripherally substituted with d⁶-metal alkynyl complexes†

Samuel Drouet,^a Areej Merhi,^b Guillaume Grelaud,^{ac} Marie P. Cifuentes,^c Mark G. Humphrey,^{*c} Katarzyna Matczyszyn,^d Marek Samoc,^{*de} Loïc Toupet,^f Christine O. Paul-Roth^{*ab} and Frédéric Paul^{*a}

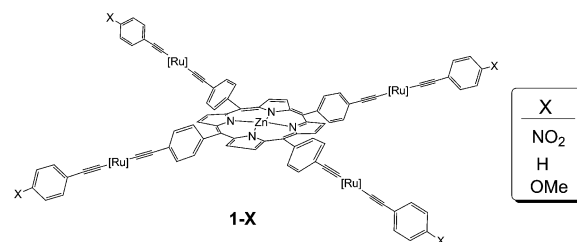
Received (in Victoria, Australia) 10th July 2012, Accepted 26th August 2012

DOI: 10.1039/c2nj40589j

The syntheses of new Zn(II) tetraphenylporphyrin (ZnTPP) derivatives functionalized with electron-rich d⁶-transition metal alkynyl complexes at their periphery are reported. Z-scan measurements reveal remarkably large effective two-photon absorption (TPA) cross-sections in the visible range for these compounds.

Molecules with significant TPA cross-sections have been attracting increasing attention over recent years because of the huge number of promising applications in emerging biophotonic and nanophotonic technologies that exploit this unusual third-order nonlinear optical (NLO) property.^{1,2} The outstanding cubic NLO properties of porphyrins were recognized very early,^{3,4} with several families of porphyrins being systematically screened for their TPA capabilities in the visible/near-IR range.^{5,6} Among the various Zn(II) derivatives examined so far, some conjugated dimers were shown to possess remarkable TPA capabilities, while the corresponding monomeric Zn(II) porphyrin derivatives are usually much poorer two-photon absorbers.^{7–10}

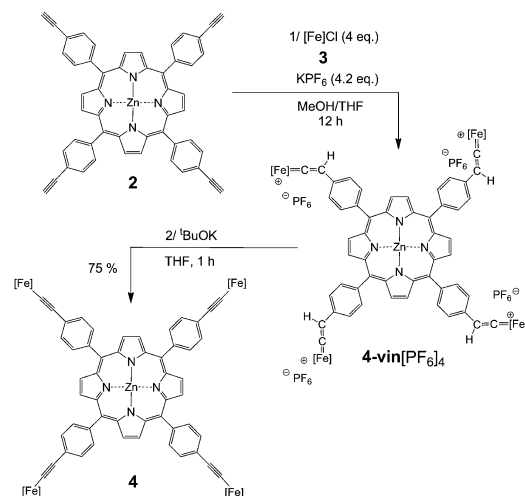
We have recently found that monomeric ZnTPP derivatives such as **1-X** (Scheme 1) exhibit quite large effective TPA cross-sections in the visible range, when peripherally functionalized



Scheme 1 Functional porphyrins **1-X** ([Ru] = *trans*-Ru(dppe)₂).

with Ru(II) alkynyl complexes.¹¹ We now report the synthesis, characterization and Z-scan studies of two additional related derivatives, and confirm that peripheral organometallic substituents can strongly influence the effective two-photon absorption properties of these novel chromophores at selected wavelengths.

The synthesis of **4** was effected in two steps, *via* a vinylidene intermediate (**4-vin**)[PF₆]₄,¹² by reacting the known tetra-alkynyl porphyrin **2**^{11,13} with the Fe(II) precursor **3**¹⁴ (Scheme 2). The tetracationic vinylidene intermediate ($\delta_P = 88.5$ ppm in the ³¹P NMR and $\nu_{Fe-C\equiv C} = 1617$ cm⁻¹ in the IR) was not



Scheme 2 Synthesis of **4** ([Fe] = Fe(η^5 -C₃Me₅)(dppe)).

^a Institut de Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France. E-mail: frederic.paul@univ-rennes1.fr

^b INSA-ISCR-UMR 6226, Université Européenne de Bretagne, INSA de Rennes, 35043 Rennes Cedex, France

^c Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia. E-mail: mark.humphrey@anu.edu.au

^d Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, 50-370 Wrocław, Poland. E-mail: marek.samoc@pwr.wroc.pl

^e Laser Physics Centre, Australian National University, Canberra, ACT 0200, Australia

^f Institut de Physique de Rennes (IPR), UMR CNRS 6251, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

† Electronic supplementary information (ESI) available: Additional experimental and crystallographic details. Procedure used for the NLO measurements. CCDC reference numbers 884562. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2nj40589j

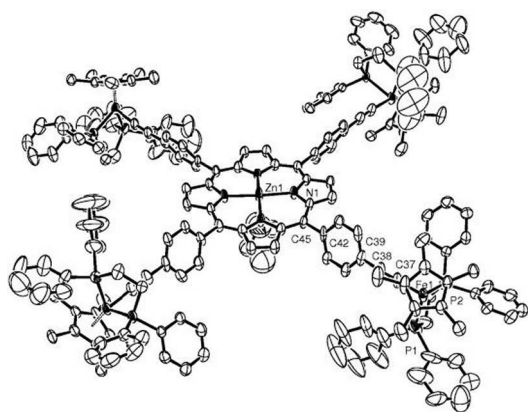


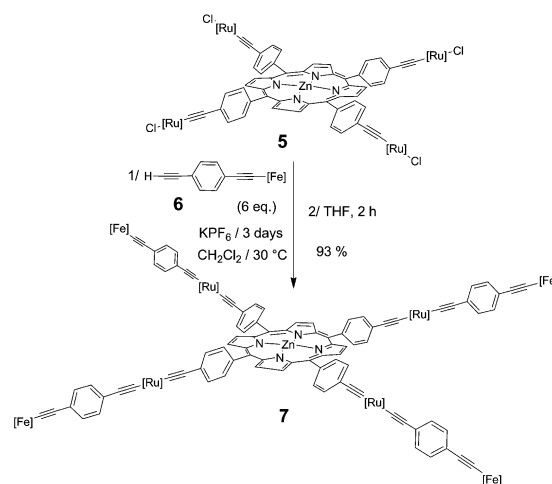
Fig. 1 ORTEP of **4** (50 % probability level). Hydrogen atoms have been omitted for clarity. A disordered Et₂O molecule coordinated to Zn is shown below the porphyrin plane.

purified, but rather was deprotonated directly after isolation to give the desired porphyrin **4** in 75% overall yield. The structure of **4** was confirmed by X-ray diffraction (Fig. 1).¹⁵ Possibly due to slow desolvation of the pentane solvates or of the Et₂O molecule coordinated to the Zn(II) atom of the porphyrin, no accurate elemental analysis of this compound was obtained, but the molecular ion peak was detected by ESI-HRMS as the di-, tri- and tetra-protonated species (ESI⁺).

In the cyclic voltammogram, the oxidation of all Fe(II) endgroups was observed as a single and chemically reversible event at -0.15 V vs. SCE (ESI⁺).¹⁶ The corresponding Fe(III) tetracation **4**[PF₆]₄ was isolated as a green solid after oxidation of **4** with four equivalents of [FcH][PF₆]. A characteristic shift to lower wavenumbers of the $\nu_{C\equiv C}$ is observed for **4**[PF₆]₄ (1989 cm⁻¹) compared to the corresponding band for **4**.¹⁷ The ¹H NMR spectrum of **4**[PF₆]₄ in CD₂Cl₂ reveals the expected Fe(III) alkynyl polyradical, with the *ortho* and *meta* protons of the *meso* phenyl groups resonating at -40.8 and 30.1 ppm, respectively, and the pyrrolic protons as a singlet near 10.5 ppm (see ESI⁺).¹⁸ The weak interaction between the unpaired electrons in this Fe-centered tetra-radical is indicated by ESR at 70 K; a rhombic spectrum was detected for **4**[PF₆]₄ ($g_1 = 2.024$, $g_2 = 2.105$ and $g_3 = 2.253$),¹⁹ while a broad and featureless signal would have been observed in the case of strong spin–spin exchange coupling.²⁰

Starting from **5**,¹¹ and from the known complex **6**,²¹ the nonametallc porphyrin **7** featuring two alkynyl complexes in each branch was also synthesized (Scheme 3).²² This compound (**7**) was isolated in good yield (93%) but, as seen with related compounds,¹³ it could not be characterized by ESI- or MALDI-MS spectroscopy. However, a consistent set of spectral signatures was obtained from IR, ³¹P and ¹H NMR, as well as diagnostic cyclic voltammograms, in which the Fe(II)- and Ru(II)-centered oxidations occur at -0.22 V and 0.44 V vs. SCE in a chemically reversible way and with equal intensities (ESI⁺).

The UV-Vis absorption spectra of **4** and **7** were recorded in dichloromethane (Fig. 2). The strong Soret band near 420 nm is the source of the green color of these compounds. This band is slightly red-shifted in **4** compared to **7** and also to **5**, the latter compounds possessing spectra closer to those of **1-X** derivatives.¹¹



Scheme 3 Synthesis of **7** ([Fe] = Fe(η^5 -C₅Me₅)(dppe) and [Ru] = *trans*-Ru(dppe)₂).

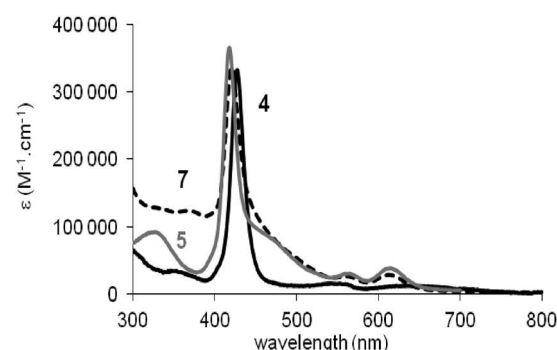


Fig. 2 UV-vis spectra of **4**, **5** and **7** (dotted line) in CH₂Cl₂.

The lowest-energy absorptions (near 550 and 620 nm) correspond to the porphyrin Q-bands; these are less intense, and blue- and red-shifted, respectively, for **4** relative to **7** and to **5**. The $d_M \rightarrow \pi_{C\equiv C}^*$ MLCT bands (M = Fe, Ru) expected in the 400–300 nm range are obscured by the other absorptions.¹⁶ The nonlinear absorption behavior of **4** and **7** were next measured in the spectral range of 600 to 1600 nm using Z-scan (ESI⁺), and were compared to those of the **1-X** derivatives (Table 1). The effective TPA cross-sections were then deduced from the imaginary part of the cubic hyperpolarizability γ . The latter exhibit a complicated wavelength-dependence, with three maxima and one minimum (Table 1), reminiscent of that previously observed for **1-X** derivatives.¹¹

Due to the centrosymmetric nature of these porphyrins, the one-photon-allowed states cannot be involved in any TPA process because of the differing selection rules.¹¹ Nevertheless, the first maximum near 1100 nm for **4** and **1-X** compounds corresponds to excited TPA states in the porphyrin core Q-bands region while the minimum near 600 nm, which occurs at the wavelength of the one-photon band at lowest energy, certainly corresponds to a saturable absorption (SA) process involving this absorption band. The second TPA maximum occurs near 710 nm, with effective cross-sections up to 10 200 GM (for **4**); in contrast to the TPA process centered at 1100 nm, the $\sigma_{2\text{eff}}$ values of the 710 nm TPA bands appear strongly influenced by the nature of the organometallic endgroups. Because the

Table 1 Extremal values of the effective two-photon absorption cross-sections (σ_{eff}) for given wavelengths^a

Cpnd	1st max		2nd max		3rd max		1st min	
	λ_{max}^b	$\sigma_{\text{eff}}^c/\text{GM}$	λ_{max}^b	$\sigma_{\text{eff}}^c/\text{GM}$	λ_{max}^b	$\sigma_{\text{eff}}^c/\text{GM}$	λ_{max}^b	$\sigma_{\text{eff}}^c/\text{GM}$
1-NO₂	530	6000 ± 500	770	6000 ± 3000	1000	1500 ± 500	620	−4500 ± 200
1-H	—	—	710	4800 ± 500	1300	1400 ± 500	595	−2800 ± 600
1-OMe	< 530	3400 ± 500	710	4200 ± 500	1000	1300 ± 100	620	−1400 ± 400
4	570	6600 ± 1000	740	10 200 ± 1000	1000	600 ± 200	650	−6100 ± 1000
7	550	8900 ± 1500	740	8000 ± 500	— ^d	— ^d	620	−1500 ± 1000

^a Measurements performed in dichloromethane. ^b In nm. ^c In Göppert-Mayer units (1 GM = $1 \times 10^{-50} \text{ cm}^4 \text{ s}^{-1}$). ^d Not determined due to sample photodegradation.

largest cross-sections are found for **4** and **7**, which possess the more electron-rich metal center (M = Fe) connected to the porphyrin core, it is tempting to ascribe the excited state at the origin of the TPA process to a centrosymmetric $d_M \rightarrow \pi_{C \equiv C}^*$ MLCT state (M = Fe, Ru),^{4,23} located at *ca.* 350 nm.¹⁶ Finally, the TPA maxima occurring at wavelengths below 600 nm, *i.e.* in an energy range where many excited states coexist, again exhibit the highest intensities for **4** and **7**. The excited states at the origin of these two-photon absorptions are more difficult to assign and necessitate calculations.

In conclusion, we report here the synthesis of two new ZnTPP derivatives functionalized at their periphery by “Fe(η^5 -C₅Me₅)-(dppe)C≡C” fragments. Moreover, we show that these new π -conjugated polynuclear assemblies incorporating electron-rich metal alkynyl fragments (**4** and **7**) exhibit TPA maxima at *ca.* 550 and 740 nm, with significantly larger effective cross-sections than analogous compounds featuring less electron-rich endgroups, such as bis-alkynyl “*trans*-Ru(dppe)₂(C≡CAr)C≡C” fragments (**1-X**). Indeed, when compared to most of the monomeric Zn(II) porphyrin derivatives investigated to date,^{7,8} much larger TPA cross-sections are found at technologically-significant wavelengths for these new organometallic derivatives, with effective cross-sections up to 10 200 GM for **4** at 740 nm. From the perspective of the practical use of TPA absorbers, the existence of a strong SA peak near 620 nm for **4** (−6100 GM) further widens the interest of this particular compound. Finally, preliminary investigations indicate that the tetracationic Fe(III) tetradical **4**[PF₆]₄ possesses significant kinetic stability; work is now aimed at assessing the potential of **4** and **7** for electro-switching their remarkable cubic NLO properties.^{22,24}

Experimental

The reactions were carried out under an inert atmosphere using Schlenk techniques. Solvents were freshly distilled under argon using standard procedures.

Compound 4

In an oven-dried Schlenk tube, (η^5 -C₅Me₅)(dppe)FeCl (**3**;¹⁴ 0.225 g, 0.360 mmol), KPF₆ (0.075 g, 0.41 mmol), and the Zn(II) porphyrin **2**¹³ (70 mg, 0.09 mmol) were suspended in a mixture of methanol and tetrahydrofuran (30 mL, v/v, 2:1) and stirred for 12 h at room temperature. After removal of the solvents, the residue was dissolved in 30 mL of dichloromethane in the presence of an excess of ^tBuOK (0.046 g, 0.41 mmol) and stirred for 2 h at room temperature. After removal of the solvent, the dark residue was extracted with

toluene and the extract concentrated *in vacuo*. Several washings with diethyl ether removed the excess of **2** and yielded the air-sensitive complex **4** as a green solid (211 mg, 75%). X-Ray-quality crystals were grown by slow diffusion of pentane into a CH₂Cl₂ solution of **4**. HRMS (ESI, MeOH-CH₂Cl₂, *m/z*): [M + 2H]²⁺ calc. for C₁₉₆H₁₈₂Fe₄N₄P₈Zn 1563.4477, found: 1563.4472 (10%); [M + 4H]⁴⁺ calc. for C₁₉₆H₁₈₄Fe₄N₄P₈Zn 782.2278, found: 782.2274 (100%). IR (ν , KBr-CH₂Cl₂, cm^{−1}): 2043/2052 (*vs.* FeC≡C). ³¹P{¹H} NMR (81 MHz, C₆D₆, δ in ppm): 101.7 (broad s, 8P, (dppe)Fe). ¹H NMR (200 MHz, C₆D₆, δ in ppm): 9.21 (s, 8H, *H* _{β -pyrrolic), 8.22 (s, 24H, *H*_{Ph/dppe} + *H*_{Ar}), 7.64 (d, 8H, ³*J*_{H,H} = 7.6 Hz, *H*_{Ar}), 7.50–7.00 (m, 64H, *H*_{Ar/dppe} + *H*_{phenyl}), 2.90 (m, 8H, *CH*₂), 1.88 (m, 8H, *CH*₂), 1.66 (s, 60H, C₅(CH₃)₅). ¹³C{¹H} NMR (125 MHz, C₆D₆, δ in ppm):¹⁵ 151.3 (s, C _{α -pyrrolic}), 139.9 (t, ³*J*_{P,H} = 38 Hz, Fe–C≡C), 139.6 (s, C_{Ar[Cd]}), 140.6 and 138.8 (2 × s, C_{i/dppe}), 136.1 (s, CH_{Ar[Cd]}), 135.4 and 135.1 (2 × broad s, 2CH_{O/dppe}), 132.8 (s, CH _{β -pyrrolic}), 131.2 (s, C_{Ar[Cd]}), 130.1 and 129.5 (2 × broad s, CH_{p/dppe}), 129.3 (s, CH_{Ar[Cd]}), 128.3 and 128.1 (2 × broad s, 2CH_{m/dppe}), 122.5 (s, C_{meso}), 121.5 (broad s, Fe–C≡C), 88.6 (s, C₅(CH₃)₅), 31.9 (m, CH_{2/dppe}), 11.3 (s, C₅(CH₃)₅). UV-vis (CH₂Cl₂, λ_{max} , (ϵ , 10³ M^{−1} cm^{−1}), nm): 351 (34), 428 (330), 537 (16), 635 (15). CV (CH₂Cl₂, 0.1 M [Bu₄N][PF₆], 20 °C, 0.1 V s^{−1}, *E*^o in V *vs.* SCE): −0.14, 0.88.}

Compound 7

In a Schlenk tube, the tetraruthenium porphyrin complex **5**¹¹ (100 mg, 0.022 mmol), the iron compound (dppe)(η^5 -C₅Me₅)-FeC≡C(1,4-C₆H₄)C≡CH (**6**;²¹ 95 mg, 0.13 mmol) and KPF₆ (24.5 mg, 0.142 mmol) were dissolved in 30 mL of dichloromethane and stirred for 3 days at 30 °C. After removal of the solvent, the green residue was dissolved in THF in the presence of an excess of ^tBuOK (11 mg, 0.01 mmol) and stirred for 3 h at room temperature. After evacuation of the solvent, the product was extracted with toluene; the solution was concentrated and washed with Et₂O to afford the complex **7** (150 mg, 0.020 mmol, 93%) as an air-sensitive green solid. IR (ν , KBr, cm^{−1}): 2047 (*vs.* FeC≡C + RuC≡C). ³¹P{¹H} NMR (81 MHz, C₆D₆, δ in ppm): 101.8 (s, 8P, (dppe)Fe), 55.1 (s, 16P, (dppe)₂Ru). ¹H NMR (500 MHz, C₆D₆, δ in ppm): 9.41 (s, 8H, *H* _{β -pyrrolic), 8.40 (d, 8H, ³*J*_{H,H} = 6.3 Hz, *H*_{Ar}), 8.12 (m, 16H, *H*_{Ar/dppe}), 7.87 (m, 48H, *H*_{Ar/dppe}), 7.57 (d, 8H, ³*J*_{H,H} = 6.6 Hz, *H*_{Ar}), 7.45–6.80 (m, 192H, *H*_{Ar/dppe} + *H*_{Ar}), 2.72 (m, 32H, CH_{2/dppe/Ru}), 2.59 (m, 8H, CH_{2/dppe/Fe}), 1.89 (m, 8H, CH_{2/dppe/Fe}), 1.59 (s, 60H, C₅(CH₃)₅). UV-vis (CH₂Cl₂, λ_{max} nm (ϵ , 10³ M^{−1} cm^{−1})): 351 (98), 424 (347), 560 (24), 614 (28). CV (CH₂Cl₂, 0.1 M [Bu₄N][PF₆], 20 °C, 0.1 V s^{−1}, *E*^o in V *vs.* SCE): −0.22, 0.44.}

Compound 4[PF₆]₄

In a Schlenk tube, **4** (150 mg, 0.048 mmol, 1.0 eq.) and [Fe(η^5 -C₅H₅)₂][PF₆] (64 mg, 0.193 mmol, 4.0 eq.) were stirred for 1 h at 25 °C in CH₂Cl₂ (15 mL). After partial removal of the solvent (*ca.* 5 mL), pentane was added (60 mL), the mixture was filtered, and the solvent was removed. The residue was then washed with thoroughly degassed toluene (2 mL) and pentane (2 mL) at 0 °C to obtain the title tetracation 4[PF₆]₄ complex as a dark green solid (89 mg, 50%). IR (KBr–CH₂Cl₂, cm^{−1}): ν = 1986/1989 (w, FeC \equiv C), 839/846 (vs. PF₆[−]). ¹H NMR (200 MHz, CD₂Cl₂): δ = 30.1 (m, 1H, CH_{Ar}[C₂]), 10.5 (s, 1H, CH _{β -Pyrrole}), 8.0 (s, 2H, H_{Ph-dppe}), 7.0 (m, 8H, H_{Ph-dppe}), 6.4 (m, 2H, H_{Ph-dppe}), 3.7 (s, 4H, H_{Ph-dppe}), 1.9 (s, 4H, H_{Ph-dppe}), −2.7 (m, 2H, CH_{2-dppe}), −10.2 (s, 15H, C₅(CH₃)₅), −40.8 (broad s, 1H, CH_{Ar}[C₁]).

X-Ray crystallography

Diffraction data frames for **4** were collected on a CCD Sapphire 3 Xcalibur diffractometer at 120(2) K using Mo–K α radiation (λ = 0.71073 Å). The structure was solved with a crystallographically imposed $\bar{4}$ symmetry by direct methods using the SIR97 program,²⁵ and then refined with full-matrix least-square methods based on F^2 (SHELX-97)²⁶ with the aid of the WINGX²⁷ program. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were then included in calculated positions. A final refinement on F^2 with 9916 intensities ($I > 2\sigma(I)$) and 522 parameters converged at $wR(F^2)$ = 0.3241 ($R(F)$ = 0.1684). Crystal data: C₂₀₀H₁₉₀Fe₄N₄O₈P₈Zn₄C₅H₁₂, M = 3490.67, tetragonal, space group I 4₁/a, a = 36.9262(5) Å, b = 36.9262(5) Å, c = 14.7933(8) Å, U = 20 171.3(12) Å³, Z = 4, T = 120(2) K, D_c = 1.140 g cm^{−3}, 124 170 reflections measured, 9916 unique (R_{int} = 0.0699) which were used in calculations. R was 0.1169 ($I > 2\sigma(I)$). The final $wR(F^2)$ was 0.3301 (all data). CCDC 884562.

Acknowledgements

The CNRS (PICS program No. 5676) UEB and FEDER (EPT grant) are acknowledged for financial support. A.M. and G.G. thank Region Bretagne for a PhD grant. M.S. and K.M. were supported by the Foundation for Polish Science Welcome grant and by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of WUT. M.G.H. and M.P.C. thank the Australian Research Council for support, an ARC Australian Professorial Fellowship (M.G.H.) and an ARC Australian Research Fellowship (M.P.C.). The authors are grateful to F. Malvolti (UR1), F. Justaud (UR1) and M.S. Jennaway (ANU) for experimental assistance.

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